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Radionuclide and heavy metal redistribution at the former pilot-scale apatite plant in Sokli, northern Finland

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A new phosphate mine is being planned at Sokli in northern Finland. In the late 1970s, pilot-scale mining and mineral processing took place at the site. The mobilisation of radionuclides and heavy metals from the mill tailings was examined in order to assess the potential environmental impact of past and future mining activities. Given the considerable amount of apatite still present, the waste material does not represent true tailings. Variations in abundance probably represent material discharges to the tailings rather than mobilization of the elements from the tailings themselves. No indication of heavy-metal migration was found. Extraction results suggest that only a small proportion of cadmium is in exchangeable form. Elements that are partly soluble under weakly-acidic conditions include copper, zinc, cadmium, uranium and lead. However, most of the elements are tightly bound to the sample matrix and therefore not easily released to the environment.

Introduction

The Sokli complex in northern Finland is the westernmost known deposit in the Devonian Kola Alkaline Province (KAP) and was discovered by Rautaruukki Oy in 1967. In addition to viable phosphate, the carbonatite massif hosts other potentially commercial deposits, including those containing niobium, iron and vermiculite. Apatite and, particularly niobium, ores are known to exhibit elevated uranium and thorium concentrations (Solatie *et al*. 2010).

Pilot-scale mining and mineral processing took place at Sokli up to the end of the 1970s. Processing of ore is not thought to have included chemical treatment but was limited to removal of gangue minerals by physical methods. Mill tailings were deposited adjacent to the enrichment facility. Today, there are plans to re-open the mine with production of around 2 million tonnes of phosphorous concentrate per year. Total mining is estimated by the Yara International at 4–10 million tonnes per year over a period of 20 years for the richest phosphorus ores and longer

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for poorer parts of the deposit. Mining activities would include open cast extraction and treatment, crushing and grinding (YVA 2009). This scheme has raised considerable public concern in the region because of the perceived environmental impact. The aim of this study is to examine the mobilisation of radionuclides and heavy metals from the mill tailings over the 40 years since Sokli ceased operation in order to assess the likely environmental consequences of any future activities for beneficiation of the phosphate ore.

In the mining process, phosphate minerals are first separated from clays and sand by washing, with the mill tailings directed to impoundment ponds. The partitioning of natural series radionuclides and heavy metals between phosphate concentrates and tailings will depend upon the type of ore as well as the methods of production (Lottermoser 2003, YVA 2009). Generally, phosphate ores from northern Finland and northwestern Russia are less radiogenic than those from, for example, the Middle East or North Africa (IAEA 2013). Additionally, mill tailings derived from physical removal of gangue at an early stage of the mining process, as discussed here, are usually less problematic than those arising from the production of phosphoric acid. The latter produces large quantities of phosphogypsum waste, which can lead to contamination of soil and groundwater (IAEA 2013).

Most of the heavy metals present at Sokli (e.g. Zn, Cu, Ni, Cr) are essential trace nutrients for plants and animals but become toxic at high concentrations; some species of these metals can be toxic even at low concentrations. Others (e.g. Cd, Hg, As, Pb, U, Ra, Th) have no known biological function. Over time, the behaviour of these pollutants in the mill tailings will be influenced by environmental processes such as surface or groundwater leaching and the ambient conditions, including pH, temperature, redox potential and the presence of organic matter. As a result, dissolved radionuclides and heavy metals may persist in solution, precipitate or co-precipitate with other components in the tailings or be adsorbed onto solid phases such as silicates, organic matter or metal oxides. Processes which act to keep contaminants in solution include leaching by residual process chemicals, microbial action and dissolution of Fe and Mn oxy-hydroxides. The degree to which each contaminant is mobilised depends on the type of ore (mineralogy, depositional environment, host rock, etc.) and the milling process (Dreesen and Williams 1982, Landa 1999, Lottermoser 2003). If heavy metals and radionuclides are mobilised from the mill tailings, they may contaminate local water courses and pollute drinking water. Other potential exposure pathways include dust dispersion and bioaccumulation through the food chain; Sokli is in an area of reindeer husbandry and foraging for berries and mushrooms is common among the local population.

Material and methods

Site description

Sokli is located in the northeastern part of the municipality of Savukoski (67°48´N, 29°18´E, 20 m a.s.l.) close to the headwaters of the Nuorttijoki and within the catchment of its tributary Soklioja. The Nuorttijoki flows to a lake, Nuorttijärvi, in Russia. The site is located 100 km from the centre of Savukoski and the border of Russia is 12 km to the east. The nearest similar deposits are Kovdor, Afrikanda and Lovozero in Russia (Fig. 1).

The region belongs to the northern-boreal vegetation zone. The climate is cool temperate: July and February mean temperatures are 13 °C and –14 °C, respectively. The mean annual precipitation is ca. 500 mm.

The main geological features of the Sokli carbonatite complex have been described by Vartiainen (1980). The thickness of the regolith varies irregularly, having a maximum of 72 m and an average of 25 m (Vartiainen 1989). Weathering of the carbonatite is associated with pronounced mineralogical changes, principally, complete dissolution of carbonates, replacement of phlogopite by vermiculite, alteration of pyrochlore and removal of sulphides. The Sokli regolithic phosphate ore has survived the erosional action of the continental ice sheet due to sheltered position in a depression formed in deeply weathered rocks within a continental ice-divide area (Helmens *et al*. 2000, O'Brien *et al*. 2005).

Fig. 1. Principal deposits of the Kola Alkaline Province.

The phosphate ore developed from the carbonatite has undergone complex weathering, leaching, recrystallization and lithification processes driven by the prevailing tropical climatic conditions [Finland was on the equator ca. 400 Ma ago, age of the intrusion ca. 365 Ma (Vartiainen 1980)]. The end product is a reddish-brown layer, averaging 26 m in thickness, which varies from solid rock to soil (Lehtinen *et al*. 2005, O'Brien *et al*. 2005).

Sampling and sample preparation

Samples of apatite ore and mill tailings were collected in 2010. Ore samples (later referred to as 'O' with sample numbers) were collected within the former mining area (WGS84 coordinates 67°48.691´N and 29°16.674´E) from nine piles consisting of apatite ore that had been mixed and crushed during processing in the late 1970s by Rautaruukki Oy. Samples of mill tailings

Fig. 2. Tailings pond. The abandoned enrichment facility can be seen behind the birch forest that has established itself on the slurry field.

Fig. 3. Tailings sample locations (National Land Survey of Finland).

(MT) were collected from a tailing pond near the enrichment facility (Fig. 2) at the northern edge of the tailing site. Two samples were taken from each location: one from the surface (referred to as T in the sample codes) and the other from 30–50 cm below the ground surface (referred to as B in the sample codes), except for sampling point 6 where only a surface sample was obtainable. The sampling transect was approximately 200 m long and the distance between sampling points, 30–40 m (Fig. 3).

Ore and mill tailing samples were dried at 40 °C for one week. The ore samples were ground to a fine powder using a Mixer Mill Type MM-2. Samples of the mill tailings were already of sufficiently small grain size (< 2 mm). The samples were digested in concentrated nitric acid in a microwave (MARS Xpress) prior to

determination of uranium, thorium and heavy metals by inductively coupled mass spectrometry (ICP-MS) and uranium and thorium by alpha spectrometry, respectively. Nitric acid was chosen based on comparative digestion experiments performed earlier on the same materials (Tuovinen *et al*. 2014). The acids used were all suprapur grade (Merck), suitable for ICP-MS. After cooling, the digest was filtered through a 0.45 μm polypropylene filter. The microwave digests were stored in Nalgene containers in a refrigerator for further analysis.

Analytical methods

Three samples, each of both ore and tailings, were analysed by X-ray diffraction (XRD) in order to identify the main minerals present. Analyses were performed using a Philips X'Pert MPD diffractometer and spectra recorded in the range 2–70° 2θ (step size 0.02° θ, time per step 1 s). The principal phases present were identified with the PANalytical X'Pert HighScore Plus program using the ICDD pdf-4/minerals database. Fractions of the major components were derived from the intensities of the diffractions peaks and are thus only semi-quantitative.

The above ore samples and two mill tailing samples were also analysed by electron probe micro-analyser (EPMA) in order to identify uranium- and thorium-bearing minerals. Analyses were performed by wavelength-dispersive spectroscopy using a Cameca SX100 instrument at the Geological Survey of Finland, Espoo. Analysing conditions were as follows: accelerating voltage = 15 kV, beam current and diameter 10 nA and 1–5 μm, respectively. Natural minerals and prepared metals were employed as standards. Analytical results were corrected using the PAP on-line correction program (Pouchou and Pichoir 1986).

The elemental compositions of ores and mill tailings were determined in solutions from the microwave digestions by Agilent 7500 ce/cx Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The resulting spectra were analysed using a Masshunter spectral analysis software. Elemental standard solutions were prepared by diluting single-element standard solutions (Merck) with 5% HNO_3. Water used in preparation of dilute nitric acid was purified using a Milli-Q water purification system (Millipore, USA). For quality assurance, two reference water samples were included in the ICP-MS analysis: Environment Canada, Certified Reference Materials, Trace Element Fortified Calibration Standards, TM-27.3, lot 0510 and TMDA-64.2, lot 1010.

Gamma spectrometry was used for estimation of natural uranium and thorium series isotopes from dried samples. ^{238}U was measured with the aid of gamma emission of the progeny nuclide ^{234m}Pa in equilibrium with ^{238}U. Correspondingly, ^{228}Ra was obtained from its daughter ^{228}Ac (Beddow *et al*. 2006). ^{226}Ra was determined directly from the emission at 186 keV and with the aid of the progeny nuclides ^{214}Pb and ^{214}Bi assumed to be in secular equilibrium with their progenitor. ^{228}Th was determined using progeny nuclides ^{208}Tl and ^{212}Pb. ^{232}Th can also be estimated from ^{228}Ac, assuming secular equilibrium with ^{228}Ra, though the assumption is more tentative (Read *et al*. 2013). In order to prevent the escape of radon and thus ensure the attainment of radioactive equilibrium between ^{226}Ra and ^{214}Pb/^{214}Bi, as well as between ^{228}Th and ^{208}Tl/^{212}Pb, the samples were sealed in vacuum bags for three weeks. The samples were counted on a Canberra BE5030 HPGe detector with cryostatic cooling (CP-5F-RDC-6) and Gemini auto-sampling (FWHM 5.9 keV, 386 eV, 122 keV, 628 eV, 1332.5 keV, 1.767 eV). Prior to analysis, the detector was calibrated with a mixed nuclide standard (NPL) of similar geometry and density (washed sand, Thermo Fisher). This method has been accredited by UKAS in accordance with International Standard ISO/IEC 17025:2005 General Requirements for the Competence of Testing and Calibration Laboratories. The spectra were analysed using a Gamma99 spectral analysis software.

Uranium and thorium isotopes were also measured by alpha spectrometry after separation from microwave digests using anion exchange chromatography: uranium was first separated in 9M HCl and then thorium in 8M HNO_3 (Juntunen *et al*. 2001). The radiotracers used for determination of chemical yield in uranium and thorium separations were ^{236}U and ^{229}Th, respec-

tively. The alpha spectrometric measurements were performed with PIPS semiconductor detectors of 600 mm^2 active area, housed in Alpha Analyst model 7200-08.

A two-step sequential extraction was performed in order to study the geochemical association of metals and radionuclides in the ores and mill tailings. Three samples of both the ore and mill tailings were taken. A sample from each extraction was analysed to determine metal content by ICP-MS. The steps and the targeted forms were as follows:

Fraction 1. Exchangeable. The first step was carried out using NH_4Cl instead of the more commonly used $MgCl_2$ (Virtanen *et al*. 2013). In this step, 30 ml of 1 M NH_4Cl at pH 5.5 was added to 2 g of the solid sample. The mixture was shaken for 1 h at room temperature. The solution was then separated from the solid sample by centrifugation at 7500 rpm for 15 min and filtered to 0.25 μm (polyethersulphone PES, Nalgene; Thermo Fisher Scientific, Waltham, MA, USA). The sample was washed twice with 30 cm^3 of the reagent, centrifuged and the washings added to the extracted solution.

Fraction 2. Desorbable in mild acids. In the second step, the residual solid sample from the first extraction was treated with 1 M CH_3COONH_4 (in 25% CH_3COOH) at pH 4.5, for 2 h at 50 °C. The centrifugation and washing were performed as for fraction 1 and again the washings were added to the extracted solution.

Results and discussion

Mineralogy and mineral chemistry

The main minerals present in the phosphate ore comprise apatite [$Ca_5(PO_4)_3F$], 75%; goethite [FeO(OH)]; 10%, vermiculite [$(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2$], 8% and magnetite ($Fe_3O_4$) < 5%. In one of the samples, dolomite [$CaMg(CO_3)_2$] was also found at < 5%. In the mill tailings, the main mineral constituents are: apatite, 73%; plagioclase [$(Ca,Na)Al_2Si_2O_8$], 13%; quartz, 10% and magnetite, 3%. One of the three samples also contained goethite at 10%, vermiculite at < 5%, iron columbite ($FeNb_2O_6$) at < 5% and pyrochlore [$(Ca,Na)_2Nb_2O_6(OH,F)$] at < 5% (sample MT-5B). The fact that the apatite content in the mill tailings is almost the same as in the parent ore reveals that the physical enrichment process performed previously failed to extract substantial amounts of apatite and therefore, the mill tailings do not represent the composition that would be obtained in an optimized full-scale, beneficiation process. The planned enrichment will not be similar; it will be based on flotation of apatite minerals.

Quantitative chemical analyses of uranium- and thorium-bearing minerals were determined by electron microprobe analysis (Table 1). The uranium- and thorium-bearing phases identified comprise pyrochlore (pyrochlore, bariopyrochlore, thoriopyrochlore and uranpyrochlore) and monazite-group (monazite and cheralite) minerals (Fig. 4). The highest thorium content was found in cheralite (up to 41.6% ThO_2), whereas in pyrochlore, ThO_2 contents varied between 0.5 and 12.0 wt%. The highest uranium content was found in uranpyrochlore (4.0% UO_2); UO_2 content in cheralite varied between 0.9 and 1.3 wt%. Crystal form is euhedral to subhedral suggesting that no or little leaching has taken place.

According to thermal neutron induced fission track studies by Rehtijärvi and Lindqvist (1978), uranium is also bound in apatite, fine-grained goethite and altered magnetite. In our study, however, the detection limit for uranium (0.2% UO_2 by microprobe analysis) was too high to quantify the uranium content in these phases. We may, however, assume that apatite will be a significant host for uranium in addition to pyrochlore and monazite group minerals.

Trace elements in Sokli ore and mill tailings

In the case of As, Cd and Ni, their concentrations were the same in the ore and the mill tailings, and all were within the range of analytical uncertainty (Table 2). Thus, no concentration of these elements during ore processing appears to have taken place. However, the concentrations of Cu, Zn, Pb and, possibly, Cr were clearly higher

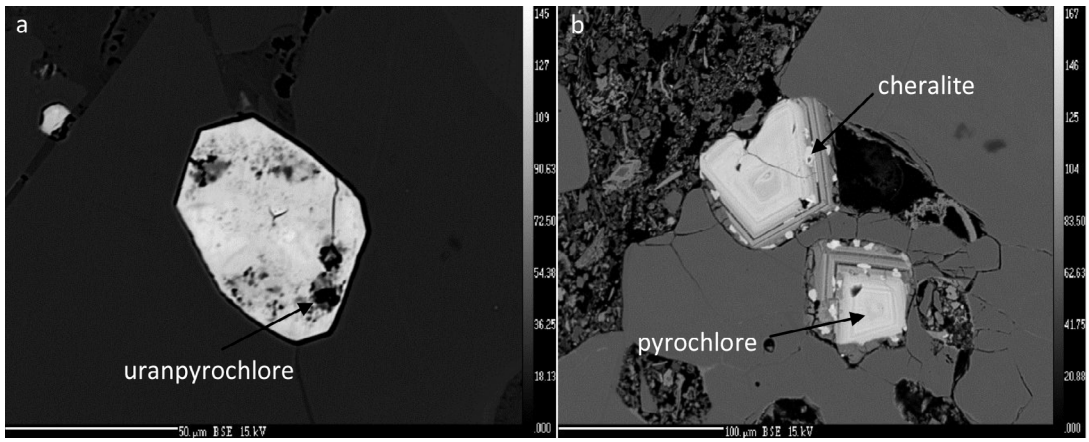

Fig. 4. Back-scattered electron image of euhedral crystals of (**a**) uranpyrochlore and (**b**) thorium-bearing pyrochlore present as inclusions in apatite. The small, light-coloured grains associated with pyrochlore are cheralite crystals.

in the mill tailings than in the ore. In the case of Hg, the opposite seems to be true, though concentrations were low and subject to analytical uncertainty. In comparison with other phosphate occurrences (Table 3), the concentrations of Cd and Cu were low in the ore samples whereas the concentrations of chromium and mercury were more typical.

Table 1. Compositions (wt%) of uranium- and thorium-bearing minerals in the Sokli regolithic phosphate ore.

	Sample and mineral						
	O-1 Cheralite	O-9 Uranpyrochlore	MT-1B Bariopyrochlore	MT-1B Bariopyrochlore	MT-1B Pyrochlore	MT-1B Monazite	MT-5B Cheralite
SiO_2	n.d	n.d.	1.56	1.97	0.08	0.15	0.30
TiO_2	0.13	3.58	3.41	2.19	5.01	0.02	n.d.
Al_2O_3	0.22	1.07	0.26	0.01	n.d.	0.34	0.11
FeO	1.93	4.53	2.97	1.33	0.61	1.44	1.28
MnO	0.22	0.03	0.04	0.09	0.05	0.09	n.d.
MgO	0.09	0.16	0.06	0.13	0.03	n.d.	0.07
CaO	13.25	4.20	2.11	0.77	17.32	7.13	12.85
Na_2O	n.d.	0.01	n.d.	n.d.	5.96	n.d.	n.d.
K_2O	0.04	n.d.	0.03	0.01	0.03	0.01	0.03
SrO	1.14	3.46	3.86	3.73	0.19	0.57	1.14
BaO	1.24	3.61	8.42	5.88	n.d.	1.12	1.48
UO_2	0.94	4.00	0.27	n.d.	n.d.	n.d.	1.30
ThO_2	41.61	0.92	5.29	3.72	0.51	0.62	38.65
PbO	n.d.	1.11	0.78	n.d.	n.d.	n.d.	n.d.
Ta_2O_5	2.30	25.67	0.77	0.53	n.d.	n.d.	0.56
Nb_2O_5	0.23	28.08	61.90	60.30	65.02	0.14	0.84
ZrO_2	n.d.	0.66	0.65	3.26	0.72	n.d.	n.d.
Y_2O_3	n.d.	n.d.	0.21	0.36	0.17	0.10	1.11
Ce_2O_3	1.08	1.97	3.07	3.85	0.94	23.94	1.10
Nd_2O_3	0.78	n.d.	n.d.	0.31	0.10	8.80	2.39
La_2O_3	1.56	n.d.	n.d.	0.11	0.14	16.43	2.58
Pr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	4.40	0.56
P_2O_5	27.19	7.26	3.30	n.d.	0.19	28.11	25.69
F	0.55	0.12	0.08	0.07	4.94	0.64	0.16
F = O	–0.23	–0.05	–0.04	–0.03	–2.08	–0.27	–0.07
Total	94.47	90.41	99.15	88.79	99.97	94.18	92.33

The concentrations of As, Pb, Zn and especially Ni, were high when compared with those in phosphate rocks from different sources. The main host for these metals is most likely apatite because its structure is characterized by various substitutions without significant alteration to its basic crystal form: $A_5(XO_4)_3Z$, where A = Ba, Ca, Ce, K, Na, Ni, Pb, Sr, Y, Zn, X = As, P, Si, V and Z = F, Cl, P, OH, H_2O (Clara *et al*. 2007, Meck *et al*. 2011).

Activity concentrations and isotopic ratios in Sokli ore and mill tailings

All samples were measured by gamma spectrometry to determine activity concentrations for ^{238}U and ^{232}Th progeny (Table 4). Uranium and thorium were also determined by ICP-MS.

The mean uranium concentration in the ore, measured by ICP-MS, was 41 ppm (range 24–52 ppm); the thorium concentration was 104 ppm (range 54–157 ppm). The corresponding values in the mill tailings were 65 ppm (range 39–86 ppm) and 171 ppm (range 85–248 ppm). These data indicate an enrichment of ~50% in the tailings. Gamma spectrometry gave nearly identical uranium concentrations for ^{238}U (^{234m}Pa): the mean ratio of uranium concentration measured by gamma spectrometry to that measured by ICP-MS was 0.97 ± 0.13. The corresponding ratio for the determination of ^{232}Th

Table 2. Trace element concentrations (ppm) in Sokli ore and mill tailings (9 samples). n.d. = not determined.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Ore								
Mean	35	2	76	7	11	694	28	64
Range	22–52	1–4	37–126	< 2–34	1–45	564–1030	13–44	< 2–204
Mill tailings								
Mean	35	5	116	48	< 1	747	56	519
Range	25–49	3–7	68–250	< 2–86	n.d.	683–860	30–76	128–844

Table 3. Trace elements (ppm) found in phosphate rocks. – = not reported.

Trace elements	CEI (Russia)[a]	South Africa (Palabora)[a]	Morocco (Khouribga)	USA Florida	Senegal	Sokli (Finland; this work)
As	10	13	13	11	18	35
Cd	1.2	1.3	15	9	53	2
Cr	19	1	200	60	6	76
Cu	37	–	40	13	–	7
Hg	33	0.1	0.1	0.02	0.2	11
Ni	2	–	35	28	–	694
Pb	–	–	10	17	5	28
Zn	20	6	200–400	70	–	64

[a] igneous; the remainder is sedimentary in origin.

Table 4. Mean activity concentrations (Bq kg^{-1}) of ^{238}U, ^{232}Th and selected progeny nuclides in Sokli ore and mill tailings measured by gamma spectrometry (±5% uncertainty).

	^{234m}Pa(^{238}U)	^{214}Pb/^{214}Bi(^{226}Ra)	^{228}Ac(^{232}Th)	^{208}Tl/^{212}Pb(^{228}Th)	^{228}Ac(^{228}Ra)
Ore (n = 9)					
Mean	483	414	659	734	665
Range	356–670	336–606	450–724	458–859	455–733
Mill tailings (n = 11)					
Mean	730	686	677	778	682
Range	466–996	437–891	406–931	478–1081	408–936
Mill tailings/ore ratio	1.51	1.66	1.03	1.06	1.03

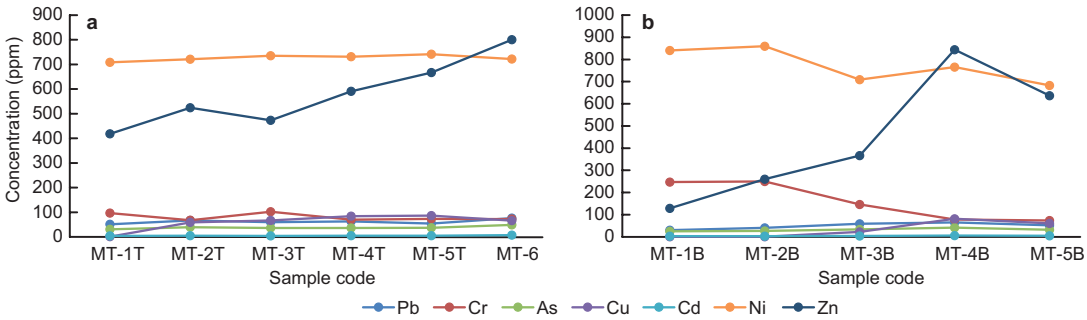

Fig. 5. Concentrations of trace metals in samples taken from the (**a**) surface and (**b**) subsurface of Sokli mill tailings along a 200 m transect.

with these two methods was 1.15 ± 0.27 assuming secular equilibrium with progeny.

Within analytical error, no fractionation between ^{238}U and ^{226}Ra could be seen. Both were enriched to a similar degree in the mill tailings.

Three ores and four mill tailings samples were analysed for their uranium and thorium isotopes by alpha spectrometry, after separation by anion exchange chromatography. The nuclides determined were: ^{238}U, ^{234}U, ^{232}Th, ^{230}Th and ^{228}Th (Table 5). The isotopic ratios of ^{234}U/^{238}U and ^{228}Th/^{232}Th were close to unity, indicating secular equilibrium in both the ore and mill tailings. However, ^{230}Th/^{238}U and ^{230}Th/^{234}U ratios were clearly elevated, at about 1.5 ± 0.2, in all ore samples which indicates that uranium has partly mobilized from the ore. In the mill tailings, these ratios varied between 1 and 3 but no systematic differences could be seen.

Horizontal and vertical mobilization of contaminants from the tailing impoundment

Sample MT-1 was taken from the middle of the slurry field and thereafter, the distance between the samples was approximately 40 m along the probable runoff direction ending in the pond. Surface samples, referred to as T, were taken beneath the organic layer. Subsurface samples, referred to as B in the sample codes, were taken approximately 30–50 cm beneath the soil surface. No notable horizontal (from 1 to 6) or vertical (T *vs*. B) changes of concentrations could be seen except for chromium and zinc (Fig. 5). For chromium, the concentrations in the first three surface samples were lower than in the corresponding subsurface samples which might indicate horizontal migration but, since this is not seen at the other three sampling sites, this is thought improbable. No mobilisation of chromium along the assumed flow direction was apparent either since chromium concentrations did not increase towards the pond. Concentrations of zinc did seem to increase towards the pond both in the surface and subsurface samples, though further sampling is needed to confirm that substantial mobilisation of zinc from the mill tailings occurred.

In summary, little or no migration of trace metals during the last 30 years could be seen, with the possible exception of horizontal migration of zinc. Slight variations in the samples

Table 5. Isotopic ratios of ^{234}U/^{238}U, ^{230}Th/^{238}U, ^{230}Th/^{234}U and ^{228}Th/^{232}Th in the ore and mill tailings samples.

	O-1	O-5	O-9	MT-1B	MT-1T	MT-5B	MT-6
U-234/U-238	0.99	0.99	1.01	0.89	1.03	1.00	1.03
Th-230/U-238	1.65	1.43	1.45	2.93	1.62	1.00	1.50
Th-230/U-234	1.66	1.45	1.42	3.28	1.58	1.00	1.46
Th-228/Th-232	0.91	1.00	0.91	1.03	0.99	0.94	1.03

are more likely to have been caused by compositional variation of the discharges during ore processing.

In the surface and subsurface layers, activity concentrations increased when approaching the pond at the end of the sludge field (Fig. 6). ^{226}Ra increased laterally from 437 to 825 Bq kg^{-1} in the subsurface samples, but in surface samples the variation was random from 620 to 891 Bq kg^{-1}. In the case of ^{232}Th, the levels also increased laterally in the subsurface samples from 406 to 695 Bq kg^{-1}; the highest activity concentration being 768 Bq kg^{-1} in sample MT-4B. In the surface samples, activity concentrations varied from 588 to 930 Bq kg^{-1}, but no systematic change could be seen. The activity concentration of ^{238}U increased in the subsurface samples laterally from 466 to 995 Bq kg^{-1} and in the surface samples the variation was again random, from 600 to 995 Bq kg^{-1}.

There was no clear evidence for vertical migration of ^{226}Ra, ^{232}Th and ^{238}U through the profile, as indicated by the randomness of distribution and equivalence of isotopic activity concentrations in the surface samples for these nuclides. The equivalence between ^{226}Ra, ^{232}Th and ^{238}U activity concentrations could also be seen in the subsurface samples. Therefore, as in the case of trace metals and supported by mineralogical evidence, we assume the reason for variation in activity concentration across the site is compositional change in material discharges rather than subsequent mobilisation.

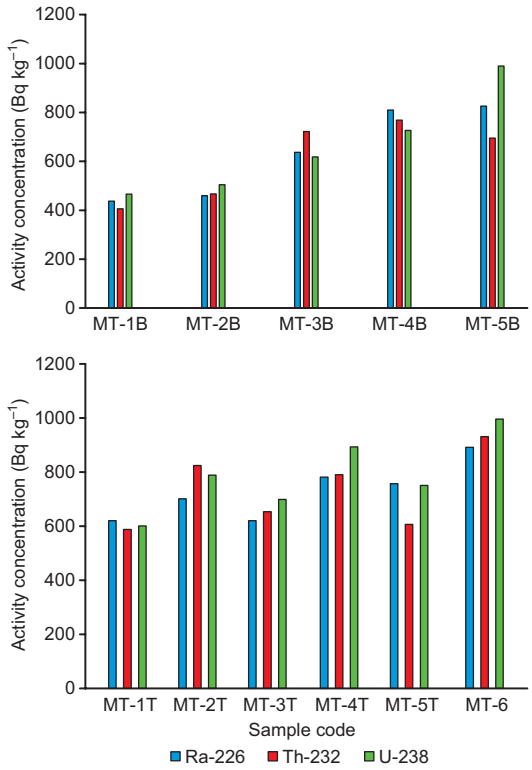

Fig. 6. Activity concentrations (Bq kg^{-1}) of radium, thorium and uranium isotopes in the (**a**) surface and (**b**) subsurface samples taken from Sokli mill tailings along a 200 m transect.

Sequential extractions

Sequential extractions were performed to determine the potential mobility of uranium, thorium and heavy metals. NH_4Cl was used to extract elements that are bound by weak electrostatic forces to mineral and organic matter surfaces whereas 1 M CH_3COONH_4 (in 25% CH_3COOH) was used to determine radionuclides and heavy metals that are soluble under weakly acidic conditions. The latter extraction is typically used to remove metals bound in carbonates but, in our case, the latter was not observed, at least not in large quantities. We describe this fraction as 'desorbable in mild acid'.

The concentrations of both arsenic and chromium (not listed in Table 6) were below the limit of detection (< 0.06 ppb) (Fig. 7). For thorium and uranium, the exchangeable fractions were on average 0.01% for uranium in both ore and mill tailings and for thorium in the ore. The corresponding value for thorium in the mill tailings was even lower, on average 0.004% (Table 6). From one mill tailings and two ore samples, thorium concentrations in the extract were below the limit of detection which was also the case for uranium in two samples of ore. The average extraction result for lead was slightly higher than that for uranium and thorium at 0.2% (0.3% in the ore and 0.14% in the mill tailings). For cadmium, the exchangeable fraction in the mill tailings was approximately 5%, and in the ore approximately 1%.

The exchangeable fraction was on average 0.08% and 0.6% for nickel and zinc, respec-

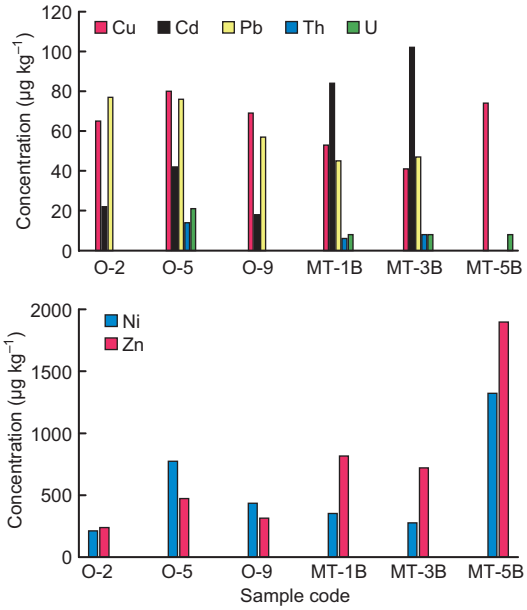

Fig. 7. Concentrations of elements in exchangeable form in the ore and mill tailings samples.

tively. For zinc, the exchangeable fraction was higher in the ore samples (0.94%) as compared with that in the mill tailings (0.18%). The concentrations of nickel and zinc appeared to increase with distance from the source (Fig. 5). This might be due to finer grain size and/or differences in mineralogy: in addition to apatite, plagioclase, quartz and magnetite, sample MT-5B also contains goethite, vermiculite, iron columbite and pyrochlore. For copper, the average exchangeable fractions as a percentage of the total concentration in the ore and mill tailings were 5.1% and 1.8%, respectively.

In summary, only a very small fraction of uranium present in these samples was exchangeable. Slightly higher fractions of the cadmium, copper, zinc and lead inventories occurred in exchangeable form but still they amounted to only a few percent of the total present.

A small part of the arsenic and chromium present (~0.4% and 0.2%, respectively), were found in the 'desorbable in mild acid' fraction although concentrations were still low (Table 7 and Fig. 8). The average concentrations for thorium were the same as in the exchangeable fractions (0.04%), implying that thorium was tightly bound in mineral phases.

The extraction result for lead was on average 1% in both ore and mill tailings samples. The results for cadmium were slightly higher than in the exchangeable fraction: 3.6% in the ore and 6.5% in the mill tailings whereas desorbable uranium was clearly higher than in the exchangeable fraction. The weakly-acidic conditions promoted oxidation of tetravalent uranium to the hexavalent form, increasing the solubility of uranium (Lehto and Hou 2011).

In the ore samples, on average 23% of zinc was desorbable in mild acid as compared with only 5.2% in the mill tailings (Fig. 9). This again suggests some mobilisation of zinc as indicated by the elemental distributions discussed above (Fig. 5).

Thus, the elements that are partly soluble in weak acid include copper (on average 11% of the total concentration), zinc (14%), cadmium (5%),

Table 6. Exchangeable fractions (%) of selected elements in the ore and mill tailings samples. For Cu, U and Th, fractions were calculated assuming initial concentrations to be half the detection limit for samples where the concentration is below the detection limit.

Sample code	Cd	Cu	Ni	Pb	Th	U	Zn
Ore							
O-2	0.70	0.2	0.02	0.20	0.0001	0.0001	0.16
O-5	1.10	8.00	0.11	0.40	0.0300	0.0400	0.70
O-9	1.80	7.00	0.05	0.40	0.0001	0.0001	1.96
Mean	1.19	5.08	0.06	0.31	0.0100	0.0100	0.94
Mill tailings							
MT-1B	2.80	5.00	0.04	0.20	0.0070	0.0200	0.05
MT-3B	2.60	0.20	0.04	0.10	0.0050	0.0100	0.20
MT-5B	8.60	0.10	0.19	0.20	0.0001	0.0100	0.30
Mean	4.65	1.77	0.09	0.14	0.0040	0.0100	0.18

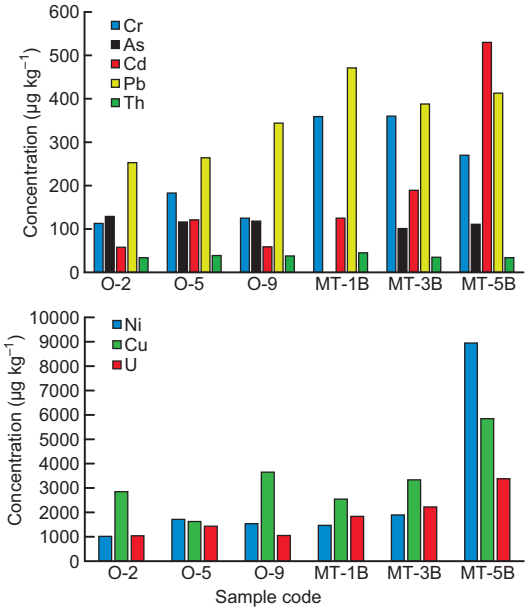

Fig. 8. Concentrations of selected elements desorbable in mild acid in ore and mill tailings samples.

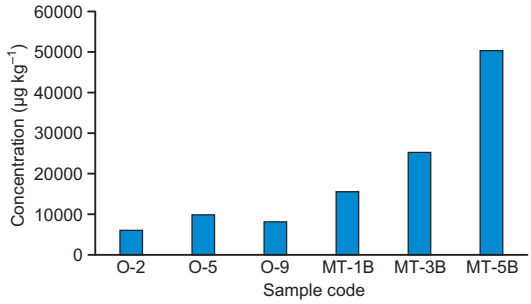

Fig. 9. The concentrations of zinc desorbable in mild acid in ore and mill tailings samples.

uranium (4%) and lead (1%). Chromium, nickel, arsenic and thorium were mainly bound to mineral phases in these samples.

Conclusions

There was no indication from mineralogical analyses that uranium or thorium was mobilised from altered pyrochlore-group minerals in the Sokli ore or tailings. From the considerable amount of apatite still present in the latter, the material did not represent actual tailings, or at least, pilot milling tests failed because apatite, the target ore mineral, was not extracted successfully from the ore.

There was no clear trend in activity concentrations for uranium, radium and thorium isotopes in the surface layers of the mill tailings. In subsurface samples, an increase in these isotopes could be seen when approaching the pond at the distal end of the sludge field. Since there was no obvious reason for lateral subsurface migration without at least some vertical mixing and, because of the equivalence of these nuclides in subsurface samples, the increase in concentrations, as in the case of trace metals, was most likely caused by compositional changes in material discharges.

Sequential extraction results suggest that a small proportion of the cadmium present (3%) was in exchangeable form and could potentially be released to the environment. Concentrations of the other elements studied in this fraction were low. Elements that are partly soluble under

Table 7. The 'desorbable in mild acid fractions' (%) in the ore and mill tailings. For copper, the initial concentrations in three samples were below detection and so the desorbable fraction could not be determined.

Sample code	As	Cd	Cr	Cu	Ni	Pb	Th	U	Zn
Ore									
O-2	0.2	2	0.1	8	0.1	0.6	0.03	3	4.1
O-5	0.5	3	0.4	< 0.01	0.2	1.3	0.07	3	14.5
O-9	0.5	6	0.1	< 0.01	0.2	2.3	0.03	4	50.9
Mean	0.4	3.6	0.2	8.4	0.2	1.4	0.04	3.2	23.2
Mill tailings									
MT-1B	0.2	4	0.1	< 0.01	0.2	1.6	0.05	5	0.9
MT-3B	0.3	5	0.2	14	0.3	0.7	0.02	3	6.9
MT-5B	0.3	11	0.2	10	1.3	0.8	0.02	5	7.9
Mean	0.3	6.5	0.2	12.0	0.6	1.0	0.03	4.3	5.2

weakly acidic conditions include copper (~11% of total concentration), zinc (14%), cadmium (5%), uranium (4%) and lead (1%). However, the bulk of the respective metal inventories were tightly bound.

At present, there is no indication that the Sokli mining site has had an impact on the surrounding area, because mill tailings were derived from physical removal of gangue at an early stage of the mining process and phosphoric acid was not produced on site.

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